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(54) PROTEINACEOUS FOODSTUFF

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for the preparation of a proteinaceous foodstuff.

For the production of various food systems oil seed proteins are often used in the form of flours, concentrates or isolates, which have been subjected to some treatment in order to remove undesirable components such as off-flavours, pigments, trypsin inhibitors and flatulence factors.

The products obtained after removal of the undesirable components are often denatured and not very useful especially in the case where a relatively high functionality is required.

There is thus a need for a process resulting in a product combining a high functionality with good organoleptic properties.

We have found a process enabling a facilitated release of pigments and off-flavour components from plane material, particularly oil-bearing seeds and especially soy.

The process according to the invention comprises:

- a) forming an aqueous slurry of defatted vegetable protein-containing material;
- b) subjecting said vegetable protein-containing material to alkaline conditions at a pH from 9 to 12, in the presence of 0.2 M to 1 M of an alkali-metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released

from the protein-containing material;
 c) separating the released pigments and off-flavour components from the protein-containing material.

The vegetable protein material is preferably originating from readily available oil-bearing seeds such as soybeans, cottonseed, sunflower, etc. Soybeans are however preferably used.

The starting vegetable protein material is defatted prior to use, using e.g. solvent extraction. Extraction with e.g. hexane gives excellent results. The aqueous slurry of the starting material is easily prepared by thoroughly mixing the defatted material with suitable amounts of water. The applied weight ratio of solids to liquid can vary within wide limits but preferably a weight ratio of solids to liquid from 1:5 to 1:30 is used.

The alkaline conditions can be obtained by using a base, preferably an alkali metal hydroxide such as sodium- or potassium-hydroxide, which can be added in solid form to the aqueous slurry or in the form of concentrated aqueous solution in a proportion sufficient to give a pH from 9 to 12 and preferably from 10 to 11.

The alkali metal halide is preferably a sodium- or potassium halide. Ideally sodium chloride is used.

The concentration of the alkali metal halide should range from 0.2 to 1 M, preferably from 0.35 to 0.70 M.

The treatment of the vegetable protein-containing material under alkaline conditions in the presence of the alkali metal halide can be performed after removal of insoluble material, mainly consisting of carbohydrates, or in the presence thereof.

We have found that an effective removal

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of off-flavour components and pigments is obtained if the treatment (step a) is carried out in the absence of the insoluble material (mainly consisting of carbohydrates), rather than in the presence thereof, in the case where the treatment of the starting material is followed by an ultra-filtration operation (step b) which is carried out in order to separate the released off-flavour components and pigments from the rest of the material. However in the case where step (b) consists of an isoelectric precipitation it is more advantageous to perform the treatment (step a) in the presence of the insoluble material.

The alkali metal halide can be added either before or after adjusting the pH of the aqueous slurry of vegetable protein-containing material to the desired value which, as already stated, lies between 9 and 12.

In some instances it has been found advantageous to first raise the pH of the aqueous slurry to a pH value within the given range and then to add the alkali metal halide.

The treatment under alkaline conditions in the presence of the alkali metal halide is carried out for a sufficiently long time to achieve a sufficient dissociation of pigments and release of off-flavour components. A suitable method for assessing the released amount of off-flavour components is GL chromatography.

The duration of the treatment and the temperature should preferably be such that the treated protein remains substantially undenatured by which term is meant that the functionality of the protein (solubility, heat-setting properties, etc) remains practically unchanged.

Usually a treatment of less than one hour and preferably from 1 to 15 minutes at a temperature ranging from 20 to 40°C will be adequate.

Anyhow the man skilled in the art will easily find the ideal conditions in each particular case.

Separation of the undesirable components such as off-flavour components and pigments from the rest of the material can be achieved by using conventional techniques. Preferably isoelectric precipitation or ultrafiltration is applied. When starting from e.g. an aqueous slurry of defatted soy flakes or soymeal isoelectric precipitation of the protein is carried out at a pH from 4.5 to 5.5, preferably at a pH from 4.5 to 4.8.

Dilution of the aqueous slurry prior to isoelectric precipitation is sometimes required to facilitate the separation of the insoluble carbohydrate and to effectively perform the isoelectric precipitation, especially if relatively high concentrations of the alkali metal halide have been used.

Depending on whether the desired end-product is a protein isolate having a protein concentration of about 90%, the isoelectric

precipitation is performed in the presence or in the absence of insoluble material mainly consisting of carbohydrates.

A preferred embodiment of the process according to the invention involves:

- i) forming an aqueous slurry of defatted soymeal;
- ii) subjecting said slurry to alkaline conditions at a pH from 9 to 12 in the presence of 0.2 M to 1 M of the alkali metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released;
- iii) diluting said mixture with water to obtain a mixture in which the molarity of the alkali metal halide is less than 0.2 M;
- iv) precipitating the protein at a pH ranging from 4.5 to 5.5;
- v) separating the insoluble material consisting of carbohydrates and protein from the liquid, to obtain a soyprotein concentrate.

Another preferred embodiment of the process according to the invention involves:

- i) forming an aqueous slurry of defatted soymeal;
- ii) subjecting said slurry to alkaline conditions at a pH from 9 to 12 in the presence of 0.2 M to 1 M of an alkali metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released;
- iii) diluting said mixture with water to obtain a mixture in which the molarity of the alkali metal halide is less than 0.2 M;
- iv) separating the insoluble material, mainly consisting of carbohydrates from the mixture to obtain a clarified protein solution;
- v) precipitating the protein at a pH ranging from 4.5 to 5.5 from the solution to obtain a protein isolate.

According to the invention the undesirable off-flavour components and pigments can be separated from the rest of the material by using ultra-filtration. Ultra-filtration can be carried out preferably after lowering the pH of the vegetable protein containing mixture from the alkaline value to a value from 6-8, by using conventional membranes having a molecular weight cut-off limit of not less than 1000 daltons and preferably not less than 5000 daltons. Depending on which end-product is envisaged (protein concentrate or protein isolate), the ultrafiltration can be carried out in the presence or in the absence of the insoluble carbohydrate.

A particularly preferred embodiment of the process according to the invention for the preparation of a soy-protein isolate involves:

- i) forming an aqueous slurry of defatted

- soymeal;
- ii) removing insoluble material, mainly consisting of carbohydrates, from said slurry to obtain a clarified solution;
 - 5 iii) subjecting said clarified solution to alkaline conditions at a pH ranging from 9 to 12 in the presence of 0.2 M to 1 M of an alkali metal halide, to obtain a mixture in which pigments and off-flavour components are substantially completely released;
 - 10 iv) lowering the pH of the mixture to a value ranging from 6 to 8; and
 - 15 v) ultra-filtering said mixture on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a soyprotein isolate.

Another particularly preferred embodiment of the process according to the invention for the preparation of a soyprotein isolate involves:

- i) forming an aqueous slurry of defatted soymeal;
- 25 ii) subjecting said slurry to alkaline conditions at a pH ranging from 9 to 12, in the presence of 0.2 M to 1 M of an alkali metal halide, to achieve a substantially complete release of pigments and off-flavour components;
- 30 iii) lowering the pH of the slurry to a value ranging from 6 to 8;
- iv) removing insoluble material mainly consisting of carbohydrates from said slurry to obtain a clarified solution;
- 35 v) ultra-filtering said clarified solution on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a soy protein-isolate.

40 A particularly preferred embodiment of the process according to the invention for the preparation of a soyprotein concentrate involves:

- 45 i) forming an aqueous slurry of defatted soymeal;
- ii) subjecting said slurry to alkaline conditions at a pH ranging from 9 to 12, in the presence of 0.2 M to 1 M of alkali metal halide;
- 50 iii) lowering the pH of the slurry to a value ranging from 6 to 8;
- iv) ultra-filtering the slurry on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a protein concentrate.
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The products obtained according to the invention can be used in several food systems and particularly in those where good functional and organoleptic performance is required, like dairy desserts, simulated meat, or fish etc.

60 The following Examples illustrate the invention.

Example I

65 *Production of a soyprotein concentrate by*

ultra-filtration

One part by weight of defatted soybean meal was mixed with 10 parts by weight of water to form an aqueous slurry. Solid sodium chloride was added to the aqueous slurry in a proportion sufficient to obtain 0.6 M dissolved NaCl. 70

The pH of the mixture was raised to 10.0 using sodium hydroxide. After 10 minutes the pH was lowered to 6.5 by adding hydrochloric acid. The mixture was concentrated two-fold in a conventional tubular module ultra-filtration plant at 55°C using a membrane cast from a solution of cellulose acetate in dimethylsulphoxide, of a molecular weight cut-off limit or more than 5,000 daltons. The inlet pressure was 90 psig. and the outlet pressure 40 psig. 75

The concentrated slurry was diluted with an equal volume of water and then reconcentrated by ultra-filtration in order to remove the sodium chloride, water soluble sugars, and other low-molecular weight impurities. This washing step was repeated until at least 90% of the low-molecular weight impurities had been removed. The concentrate obtained was spray-dried to yield a white powder containing about 70% of protein and 30% of insoluble carbohydrate. 80

Example II

Production of a soyprotein isolate by ultrafiltration 95

The procedure of Example I was followed except that the insoluble material (mainly consisting of carbohydrates) present in the acidified mixture (pH 6.5) was centrifuged off and the clarified solution was ultra-filtered to yield a protein isolate having a protein concentration of about 90%. 100

Example III

Production of a soyprotein isolate by ultrafiltration 105

The general procedure of Example II was followed except that the insoluble material was removed from the aqueous slurry before the addition of salt and sodium hydroxide. 110

Example IV

Production of a soyprotein concentrate by isoelectric precipitation

One part by weight of defatted soybean meal was mixed with 10 parts by weight of water. Sodium chloride was dissolved in the aqueous extract to give a concentration of 0.25 molar and the pH of the mixture was adjusted to 10.0 by adding sodium hydroxide. After 10 minutes the mixture was diluted with 2½ volumes of water and the pH adjusted to 4.8 by adding hydrochloric acid. The insoluble material consisting of precipitated protein and insoluble carbohydrate, was centrifuged off and spray-dried. 115 120 125

Example V

Production of soyprotein isolate by isoelectric precipitation

The general procedure of Example IV was 130

followed except that the pH was first lowered from 10.0 to 6.5, and the insoluble material, mainly consisting of carbohydrate, was removed by centrifugation before performing the isoelectric precipitation of the protein at pH 4.8.

The precipitated protein was washed once with water and spray-dried to yield a white bland protein powder with a protein concentration of about 90%.

Example VI

Preparation of a proteinaceous ingredient for meat or fish analogues

A fibrous ingredient useful for producing extended meat or fish products or full analogues was prepared starting from an isolate prepared according to Example II.

Following the procedure outlined in US Patent 3,987,213 drops of 0.05 ml of an aqueous solution containing about 25% soyprotein were added to a laminar flow of water of 94°C to coagulate the protein added. The product was collected and used for the production of 1) a seafood analogue and 2) a beef analogue.

Production of a seafood analogue

100 g. of the coagulated soyprotein were mixed with 200 ml. of a flavouring composition, pH 5.8-6.2 consisting of 3% natural seafood extracts, 1.5% seafood flavours, 0.1% salt and 95.4% water. The liquid was subsequently drained and the drained material was mixed with a dressing made of 94.9% mayonnaise, 5% tomato ketchup and 0.1% lemon juice.

Production of beef analogue

A mould was filled with collected soyprotein coagulates and the material was compressed at 550 kN/m² between paper towelling to avoid a glossy surface on the final material.

The compressed sheet of material having a thickness of 3 - 5 mm was soaked for a few minutes in a flavour/texturising bath. The sheet was drained and then heat-set in steam for 10 minutes.

When cooked in gravy and vegetables the analogue looked and could be chewed and swallowed like a slice of beef.

WHAT WE CLAIM IS:-

1. A process for the preparation of a vegetable protein product which comprises:
 - a) forming an aqueous slurry of defatted vegetable protein-containing material;
 - b) subjecting said vegetable protein-containing material to alkaline conditions at a pH from 9 to 12, in the presence of 0.2 M to 1 M of an alkali metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released from the protein-containing material;
 - c) separating the released pigments and off-flavour components from the protein-containing material.

2. A process according to claim 1, wherein the defatted vegetable protein-containing material originates from soy.

3. A process according to claim 2, wherein defatted soy meal is used.

4. A process according to claim 1, wherein the weight ratio of the solids to liquid in the slurry is from 1:5 to 1:30.

5. A process according to any one of claims 1 to 4, wherein alkaline conditions are obtained by adding an alkali metal hydroxide to the slurry.

6. A process according to any one of claims 1 to 5, wherein a pH varying from 10 to 11 is applied.

7. A process according to any one of claims 1 to 6, wherein sodium chloride is used.

8. A process according to claim 7, wherein sodium chloride is added to obtain a concentration ranging from 0.35 M to 0.70 M.

9. A process according to claim 1, wherein step (b) is performed in such a way that the protein functionality remains substantially unchanged.

10. A process according to claim 9, wherein step (b) is performed at a temperature ranging from 20°C to 40°C for a period of less than one hour.

11. A process according to claim 1, wherein step (c) consists in ultra-filtering the mixture obtained under (b).

12. A process according to claim 11, wherein the pH of the mixture obtained under (v) is lowered to a value ranging from 6 to 8 prior to ultra-filtration.

13. A process according to claim 1, which comprises

- i) forming an aqueous slurry of defatted soymeal;
 - ii) removing insoluble material mainly consisting of carbohydrates, from said slurry to obtain a clarified solution;
 - iii) subjecting said clarified solution to alkaline conditions at a pH ranging from 9 to 12 in the presence of 0.2 M to 1 M of an alkali metal halide, to obtain a mixture in which pigments and off-flavour components are substantially completely released;
 - iv) lowering the pH of the mixture to a value ranging from 6 to 8; and
 - v) ultra-filtering said mixture on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a soyprotein isolate.
14. A process according to claim 1, which comprises:
- i) forming an aqueous slurry of defatted soymeal;
 - ii) subjecting said slurry to alkaline conditions at a pH ranging from 9 to 12, in the presence of 0.2 M to 1 M of an alkali metal halide, to achieve a sub-

- stantially complete release of pigments and off-flavour components;
- iii) lowering the pH of the slurry to a value ranging from 6 to 8;
- 5 iv) removing insoluble material mainly consisting of carbohydrates from said slurry to obtain a clarified solution;
- v) ultra-filtering said clarified solution on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a soyprotein-isolate.
- 10 15. A process according to claim 1, which comprises:
- 15 i) forming an aqueous slurry of defatted soymeal;
- ii) subjecting said slurry to alkaline conditions at a pH ranging from 9 to 12, in the presence of 0.2 M to 1 M of an alkali metal halide;
- 20 iii) lowering the pH of the slurry to a value ranging from 6 to 8;
- iv) ultra-filtering the slurry on a membrane having a molecular weight cut-off limit of not less than 1000 daltons, to obtain a protein concentrate.
- 25 16. A process according to any one of claims 11 - 15 which comprises using a membrane having a molecular weight cut-off limit above 5,000 daltons.
- 30 17. A process according to claim 1, in which step (c) consists in precipitating the protein at its iso-electric point and separating the precipitated protein from the supernatant.
- 35 18. A process according to claim 17, which comprises:
- i) forming an aqueous slurry of defatted soymeal;
- 40 ii) subjecting said slurry to alkaline conditions at a pH from 9 to 12 in the presence of 0.2 M to 1 M of an alkali metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released;
- 45 iii) diluting said mixture with water to obtain a mixture in which the molarity of the alkali metal halide is less than 0.2 M;
- 50 iv) precipitating the protein at a pH ranging from 4.5 to 5.5;
- v) separating the insoluble material consisting of carbohydrates and protein from the liquid, to obtain a soyprotein-concentrate.
- 55 19. A process according to claim 17, which comprises:
- i) forming an aqueous slurry of defatted soy meal;
- 60 ii) subjecting said slurry to alkaline conditions at a pH from 9 to 12 in the presence of 0.2 M to 1 M of an alkali metal halide to obtain a mixture in which pigments and off-flavour components are substantially completely released;
- iii) diluting said mixture with water to obtain a mixture in which the molarity of the alkali metal halide is less than 0.2 M;
- 70 iv) separating the insoluble material, mainly consisting of carbohydrates from the mixture to obtain a clarified protein solution;
- 75 v) precipitating the protein at a pH ranging from 4.5 to 5.5 from the solution to obtain a protein isolate.
20. A process for producing proteinaceous foodstuffs, including meat- or fish-analogues, which comprises replacing at least part of the protein originally present by a product prepared according to any one of the preceding claims.
- 80 21. Foodstuffs produced according to claim 20.
22. A process substantially as hereinbefore described with particular reference to the Examples I-V
23. Vegetable protein product whenever 90 prepared according to a process described in any one of claims 1 to 19.

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